ABSORPTION SPECTRA OF SOLUTIONS OF AROMATIC NITRO-COMPOUNDS IN

A SOLVENT WITH FREE ATOMS OF HYDROGEN

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THE APSORPTION SPECTRUM OF AROMATIC NITRO-COMPOUND SOLUTIONS

IN SOLVENTS CONTAINING A MOBILE HYDROGEN ATOM

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In measuring the absorption spectra of nitro- and polynitrophenol solutions in liquid ammonia [1], a band displacement (spectral lines) toward the side of the long waves is noticed, as compared to the position of the bands in the spectra of aqueous nitro- and polynitrophenates. It is proposed that the reason for this phenomenon is the formation of complexes of the acid-base type, between the anion of the nitrocomposition and the solvent, which shows strong basic characteristics.

This proposition is confirmed by measuring the absorption spectra of solutions of like compounds in anhydrous hydrazine [2], where changes proved to be even more pronounced.

According to Brensted's theory, the base consists of anions of acids. The weaker the acid, the stronger the base formed by its anion.

It is known, further, that acetone occurs in two tautomeric forms — the ketonic and enolic — which are in balance with one another. The enolic form of acetone is a very weak acid [3].

It was interesting to study the absorption spectra of nitro- and poly-nitrophenates in the presence of a base such as the anion of the enolic form of acetone, and to check whether these bands, too, would align themselves with the long waves, in a manner similar to that of spectra of solutions of these compounds in liquid ammonia and in anhydrous hydrazine.

The experiments described below confirmed our assumptions and showed that alkalized acetone causes, approximately, the same changes in the spectra of nitro- and polynitrophenates, as does liquid ammonia. During experiments in our laboratory it was brought out repeatedly that aromatic polynitro-compounds easily produced colored complexes when in liquid ammonia and an-hydrous hydrazine solution. Therefore, if the formation of complexes with the solvent-base is the correct reason for the displacement of bands in the

absorption spectra of nitro- and polynitrophenates, it is probably that polynitrocompounds also form complexes with acetone anions.

As a matter of fact, Janovsky [4] observed, in 1886, that the addition of alcoholate to a solution of m-dinitrobenzene in acetone causes a violet-red coloration while taken separately, m-dinitrobenzene does not produce a colored reaction with either alkali or acetone. Wilgerodt [5] confirmed Janovsky's observations; however, Bella von Bitto [6] discovered that other ketones, as well as aldehydes, showed a similar color reaction in the presence of caustic alkali. As a result, many authors have utilized this reaction for analytical purposes (identification and quantitative determination of aromatic nitrocompounds, etc.).

It follows, from published studies, that the color reaction depends on the number and relative position of the nitro-groups and other substitutes in the benzene ring. Aromatic mono-nitrocompounds, ortho- and para-dinitro-compounds do not show a color reaction with an alkaline solution of ketone or aldehyde, which is contrary to the behavious of meta-dinitrocompounds and sym-trinitrocompounds. These latter will color an aqueous alkali solution even in the absence of ketone. The reaction will be encumbered by intro-duction of an OH or NH_2 group in ortho- or para-position relative to the nitro-group.

It is noted that this pattern corresponds to that encountered [8] in the study of solutions of aromatic nitrocompounds in liquid ammonia. The similarity is apparent in the color of solutions of like compounds in liquid ammonia and in alkalized acetone. And, furthermore, as shown in the calcu-lations below, the absorption spectra of solutions of meta-dinitrocompounds are very similar; this permits the conclusion that complexes of identical nature evolve from both solvents.

Bella von Bitto had already noticed that only ketones and aldehydes containing the $CO-CH_2$ group produced a color reaction with meta-dinitrobenzene. Reissert [9], in turn, received colored solutions through interaction, in

the presence of alkali, of meta-dinitrobenzene with benzylcyanide, with malonic acid ester, or with ester of cyanacetic acid, respectively.

From our point of view, this is explained by the fact that the enumerated compounds contain a mobile hydrogen atom and, that in the presence of alkali, anions of these weak acids are formed. These anions, being strong bases, form complexes with m-dinitrobenzene. Jackson [10] succeeded in separating, in solid form, and analyzing sodium-derivative compounds of acetoacetic ester, malonic ester, benzylcyanide, and phenol, respectively, with trinitro-benzene and trinitroanisole; Hantzsch and Kissel [11] produced a complex compound of trinitrobenzene and potassium cyanide.

We measured the absorption spectra of m-dinitrobenzene solutions in liquid ammonia, in alkalized acetone, in benzylcyanide, in ethyl ester of malonic acid, in phenylacetic acid, and in cyanacetic acid. As envisaged, the maximum of light in the absorption curves is found in the same wave length band. We therefore conclude that the structure of complexes of m-dinitro-benzene is analogous to that of substances which, at first glance, look dis-similar, but which, in reality, have on thing in common - the fact that all of them constitute bases.

In one of the studies conducted by our laboratory [8], an analogy was traced between complex forming reactions of aromatic nitrocompounds in liquid ammonia and reactions of acid-base interaction. The findings fully confirm our concept.

No one explanation can as yet be selected, among those available, to describe the mechanism of the reactions of complex formation with which we are concerned. There are arguments in favor of a mechanism which specifies the ionization of hydrogen from the benzene ring; not less probable, and, perhaps, even more so - is an aprotic electronic mechanism of the interaction (wherein the base electrons join the nitro group or the carbon atom of the benzene ring).

The outstanding characteristic of the acids discussed - and the poly-nitrocompounds are considered among them, is the fact that, as stated by Lewis /12/, their reactions with bases are specific. For example, Lewis tried to explain, in a separate paper /13/, why m-dinitrobenzene produces a complex with ammonia, but shows no reaction with caustic alkalis.

This specificity manifests itself in that m-dinitrobenzene does not react with alkali, but produces color reactions with anions of mild acids, which are obtained through action of alkali on organic substances, capable of tautomeric transformation.

The similarity of absorption spectra of solutions of meta-dinitro-compounds in liquid ammonia and in alkalized acetone, where complexes are undoubtedly formed, serves as an additional argument to support the view that the band displacement in the spectra of nitro- and polynitrophenates is also caused by the formation of molecular combinations, the concentration of which varies in solutions of different isomers.

1. Absorption-Spectra of Solutions of Nitro- and Polynitrophenates in Alkalized Acetone

Absorption spectra were obtained with a Zeiss quartz spectrograph, Chemists model (13 x 18 cubic meters). A hydrogen lamp, produced by the Government Optical Institute, served as the light source of the continuous spectrum. The lamp was fed by a current of 4 ± 0.05 amperes, which assured the necessary stability of light intensity. A bell-tube, also produced by GOI, was used as container for the solutions, which permitted variation of the thickness of the solution layer from 0.05 to 30.00 millimeters with a precision of $\pm$ 0.01 millimeter.

The bands of equal blackness were established by means of a Zeiss rapid microphotometer. The aperture of the microphotometer is 0.02 milli-meters wide, which guaranteed a precision of 2-3A for the shortwave area.

The nitro- and polynitrophenate compounds are identical with those described previously /12/.

The indicator solution was prepared as follows: To 20 milliliters of the initial solution obtained by solving a precision weighed quantity

indicator in the black flask (with 10^{-3} mols per liter), was added by means of a micro-pipette 0.1 milliliter of a water solution of KOH (0.1 N). The colorless or light-yellow solution assumed a lighter coloration, the intensity of which at first increased, then, after a few minutes became steady. In all experiments the alkaline concentration was 0.5×10^{-3} N.

The effect of the alkaline concentration on the spectrum was not studied. As shown by preliminary tests, the presence of traces of water could somewhat affect the form of the absorption curve, but would practically have no effect on the location of the maximum.

The area of the continuous acetone absorption begins near $320 \, m\mu$. Therefore, the short wave part of the spectra of solutions in acetone could not be gaged.

The p-nitrophenol and 2,4-dinitrophenol solutions are yellow; the 0-nitrophenol, 2,6-, 3,5-dinitrophenol and picric acid solutions are yellow-orange; the m-nitrophenol and 2,5-dinitrophenol solutions have an orange coloration.

In Figures 1 - 8 there are compared light absorption curves of solutions in alkalized acetone, in liquid ammonia, in anhydrous hydrazine, and in 0.005 N aqueous solution of alkali.

Table 1 contains data with regard to the position of the maximum ($\lambda m\mu$) on the absorption curves of solutions in alkalized acetone, and the logarithm value point of maximum, as well as the differentials which express the displacement of spectral bands of acetone, ammonia, and hydrazine solutions in relation to their position in the spectra of solutions in dilute aqueous alkali.

Accuracy of the date is limited by errors in the graphic interpolation (Figures 4,5 and 6).

TABLE 1

SUBSTANCE	Acetone + NaOH		Displacement of the Band $\Delta\lambda m\mu$			Change of Logarithm Coeff. of Absorptions $(\Delta lg\lambda)$		
			$(CH_3)_2CO$ NaOH	NH_3	N_2H_4	$(CH_3)_2CO+$ NaOH	NH_3	N_2H_4
p-Nitrophenol	416	4.49	19	36	43	0.26	0.26	0.67
o-Nitrophenol	428	3.74	16	28	53	0.08	0.10	0.39
m-Nitrophenol	435	2.97	45	84	120	-0.24	-0.25	0.24
2,4-Dinitrophenol	370	4.17	9	12	11	-0.01	-0.13	0.26
	422	4.16	27	32	105	0.12	0.05	0.19
2,5-Dinitrophenol	347	3.39	65	73	68	-0.51	-0.45	-0.30
	485	3.78	47	60	67	0.15	0.22	0.57
2,6-Dinitrophenol	458	3.98	28	40	10	0.16	0.15	0.43
3,5-Dinitrophenol	435	3.33	35	50		-0.07	0.01	
Picric Acid	375	4.10	17	20		-0.04	0.00	

In the absorption-spectra of nitro- and polynitrophenates, alkalized acetone causes the same type of changes as do liquid ammonia and aqueous hydrazine, but the terms of expression are weaker (with alkali of same concentration as used by us). The changes in absorption intensity closely approximate those determined for solutions in liquid ammonia. (Figure 7)

In alkalized acetone, as in the rest of the solvents, the highest displacement - among spectra of mononitrophenates - is achieved in the spectrum of m-nitrophenates. (Figure 8)

Separation of the spectral band of 2,4-dinitrophenate is caused by displacement of its long wave component. In all solvents the short wave maximum is placed almost identically. The distances between the two maximums is $52 m\mu$ for alkalized acetone, $54 m\mu$ for liquid ammonia, and $128 m\mu$ for anhydrous hydrazine.

The spectra of 2,5-dinitrophenate in acetone and ammonia are very

similar. But they, as well as the spectra of 2,6-dinitrophenate in picric acid, when compared to spectra of solutions in hydrazine, show considerably lower intensity.

2. **Absorption Spectra of Solutions of Meta-Dinitro Compounds in Liquid Ammonia and Alkalized Acetone**

Absorption spectra of meta-dinitro compound solutions were measured with a Koenig-Martens spectrophotometer. For solutions in liquid ammonia the earlier mentioned container $/14/$ was used, while a Bell-tube was employed for solutions in acetone. The meta-dinitro compound used was prepared by the Kalbaum firm.

In view of the differing intensity in coloration of solutions in liquid ammonia and in alkalized acetone, and in order to facilitate the measuring, solutions of unequal concentration were prepared with both solvents. Coloration intensity of alkalized acetone solutions depends on the concentration of the alkali. A constant concentration of alkali equal to $0.5 \cdot 10^{-3}$ mols per liter was maintained in all experiments.

The color of solutions of the same substance in both solvents is very similar, but changes as time goes on. For example, the color of 2,4-dinitrotoluene in alkalized acetone changes from blue to lilac, and then turns pink. The spectrum of every solution was photographed three times: Immediately upon preparation, after 4 hours, and again after 28 hours. It was noticed that absorption intensity as well as the form of the curve vary, while the location of the maximum remains almost unchanged. Therefore, even though measurement of spectra requires some time, it can be concluded that the position of the maximum found corresponds to its location in the spectrum of the complex which had formed, initially, in the solution.

In Figures 9 - 12 are reproduced absorption spectra of solutions of m-dinitrobenzene, 2,4-dinitrotoluene, dinitroxylene, and 2,4-dinitroanisole, in both solvents. On the ordinate axis are marked off the relative changes in absorption intensity of the solutions $\lg \epsilon_\lambda$ at a concentration of the solutions at which measurements were carried out, and not the true absorption

- 7 -

coefficients q_ε since these solutions do not conform to Beer's Law.

Table 2 indicates the initial color of the solutions, position of the maximum on the light absorption curves of solutions in liquid ammonia and in alkalized acetone, as well as the displacement of the maximum in relation to its position in the spectrum of the m-dinitrobenzene solution.

TABLE 2

SUBSTANCE	COLOR OF SOLUTION	POSITION OF MAXIMUM $(m\mu)$		DISPLACEMENT OF MAXIMUM $(m\mu)$	
		Liquid NH_3	$(CH_3)_2CO+$ $+NaOH$	Liquid NH_3	$(CH_3)_2CO+$ $+NaOH$
Dinitroxylene (melting point 90 degrees Centigrade)	Blue-Green	635	652	80	84
2,4-Dinitrotoluene	Blue	558	578	3	10
1,3-Dinitrobenzene	Lilac	555	568		
2,4-Dinitroanisole	Violet	539	555	16	13

(Followed by Figures 10 and 11)

Since the spectra change in time, the measurements did not call for great precision. A close resemblance between spectra of meta-dinitro compound solutions in liquid ammonia and in alkalized acetone is evident from the graphs and tables. Introduction of substitutes in m-dinitrobenzene causes like changes in the spectra of solutions in both solvents. This decidedly confirms the analogous structure of complexes of meta-dinitro compounds and the bases - ammonia and anions of the enolic form of acetone; it also agrees with our interpretation of the Janovsky reaction. (Figure 12)

3. <u>Absorption Spectra of Complexes of m-Dinitrobenzene with Anions</u>

   <u>of Weak Acids</u>

To obtain anions of organic solvents with a mobile hydrogen atom, metallic sodium was dissolved or, in certain cases, an alcoholic solution of sodium ethylate was added, keeping the quantity of added alcohol at a minimum. The concentration of the m-dinitrobenzene solution was 10^{-3} mols per liter. The alkali concentration was constant in all experiments, and equalled 0.5 · 10^{-3} mols per liter. (Figure 13)

To conserve space, we will not show here the spectra of each individual substance in solution, measured at various times after preparation of the solution. As a rule, the absorption intensity drops in time, and the curves run almost parallel one under the other.

In Figure 13 are compared curves of absoption spectra of m-dinitrobenzene solutions in liquid ammonia and in acetone, in ethyl ester of malonic, of phenylacetic, and of cyanacetic acids, and in benzyl cyanide, containing anions of these weak acids.

These measurements which lay no claim to great accuracy show that the maximum on absorption curves of m-dinitrobenzene solutions in such diversified agents, is always located in the same region of the spectrum $560 \mp 10\,m\mu$.

All solutions are of lilac or red color. From qualitative experiments it is known that this is also the color of solutions of m-dinitrobenzene in the presence of fluorene and malononitrile in alcoholate. Unfortunately, the irreversible changes in these solutions occur with such rapidity that measurement of the spectra is impossible. The structure of m-dinitrobenzene complexes evolving from these solutions is undoubtedly similar.

<u>Conclusions</u>

1. Absorption spectra in the ultraviolet range of para-, ortho-, meta-nitrophenol, 2,4-; 2,5-; 2,6-; 3,5-dinitrophenol, and picric acid solutions in alkalized acetone were measured. It was proved that alkalized acetone

will cause approximately the same changes in the nitro- and polynitrophenate
spectra, as liquid ammonia.

2. Absorption spectra in the visible range of m-dinitrobenzene, 2,4-
dinitrotoluene, dinitroxylene, and 2,4-dinitroanisole solutions in liquid
ammonia and in alkalized acetone were measured. The maximum on light-
absorption curves of solutions containing like substances is found in the
same range of the spectrum. The introduction of substitutes in m-dinitro-
benzene causes analogous changes in the spectra of solutions in liquid
ammonia and alkalized solutions.

3. Absorption spectra in the visible range of m-dinitrobenzene solutions
in ethyl ester of malonic acid, in ethyl ester of cyanacetic acid and in
benzylcyanide, containing anions of these weak acids, were measured. Spectra
of these solutions, as well as spectra of m-dinitrobenzene in liquid ammonia
and alkalized acetone are characterized by a maximum in the $560 \pm 10 \, m\mu$ range.
This indicates analogous structure of colorated complexes.

4. Results obtained confirm the correctness of interpretation regard-
ing the complex-formation of aromatic nitro compounds in liquid ammonia as
being reactions of the acid-base type.

In organic solvents containing a mobile hydrogen atom, examined in this
paper, the bases are constituted by anions of very weak acids.

A rational explanation of the Janovskiy reaction has been presented.

5. Comparison of absorption spectra of nitro- and polynitrophenate
solutions in alkalized acetone, liquid ammonia, and anhydrous hydrazine
strengthens the theory that the band displacement in the absorption spectra
of these compounds is caused by the fact that complexes form with the bases.

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- 10 -

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